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Plasticity in the Supercooled Liquid Region of Bulk Metallic Glasses

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INTRODUCTION

Intensive efforts have been carried out over the past decade to develop means to slow down the phase transformation kinetics during the forming of metallic glasses. As a result of these efforts, some metallic glasses can now be fabricated in bulk forms (BMG) from the liquid state at cooling rates on the order of 1–10 K/s, which is close to that of conventional casting. This enables the production of bulk amorphous alloys with a thickness of ~10 mm. While advances in amorphous metallic alloy development have been impressive, they have been made largely through experience [1].

Bulk amorphous alloys have many potential applications resulting from their unique properties. Among them it is worth mentioning: superior strength and hardness [2, 3], excellent corrosion resistance [4], shaping and forming in a viscous state [5, 6], reduced sliding friction and improved wear resistance [7], and low magnetic energy loss [8]. These properties should lead to applications in the fields of near-shape fabrication by injection molding and die casting, coatings, joining and bonding, biomedical implants, soft magnets for low energy loss, and synthesis of nanocrystalline and composite materials.

The mechanical behavior of metallic glasses is characterized by either inhomogeneous or homogeneous deformation. Inhomogeneous deformation usually occurs when a metallic glass is deformed at room temperature (i.e. low temperature) and is characterized by the formation of localized shear bands, followed by the rapid propagation of these bands, and sudden fracture. Consequently, when a metallic glass is deformed under tension it exhibits only limited macroscopic plasticity. Despite a limited macroscopic plasticity, local strain within these shear bands can be, sometimes, quite significant. These bands are typically 20–30 nm in width and may be associated with deformation-induced crystallization [9]. Whereas there exist many different views on inhomogeneous deformation in metallic glasses [10, 11]), there is no universal agreement. This paper will address only homogeneous deformation.

In the case of homogeneous deformation in metallic glasses, it usually takes place at high temperatures ($>0.70T_g$), and the material can often exhibit a significant plasticity. The transition temperature T_{tr} from the inhomogeneous to homogeneous deformation (or brittle-to-ductile transition) is, as expected, strongly dependent upon strain rate. For example, T_{tr} for $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ alloy is about 533K (corresponds to $0.82T_g$) at $5 \times 10^{-4} s^{-1}$, but it is 652K (corresponds to $1.0T_g$) at $5 \times 10^{-2} s^{-1}$ [12], suggesting that homogeneous deformation is associated with some diffusional relaxation processes (even below T_g). In the following section we divide the homogeneous deformation of metallic glasses into two regions ($T < T_g$ and $T_g < T < T_x$) for discussion purpose.

$T < T_g$

Mulder *et al* [13], in a study of the deformation of $Fe_{40}Ni_{40}B_{20}$ metallic glass in tension at elevated temperatures, found that the transition temperature from inhomogeneous to homogeneous deformation occurred at about 480–525K (0.68 – $0.75 T_g$). They also conducted creep experiments at temperatures (523–548K) below the glass transition temperature with a relatively high stress (> 1.0 GPa). Experimental results showed that the stress exponent was rather high ($n=8.5$). The activation energy was determined to be between 250 and 280 kJ/mol, which is similar to that for eutectic crystallization below the glass transition temperature.

Taub and Luborsky [14] carried out tensile creep experiments with amorphous $Fe_{40}Ni_{40}P_{14}B_6$ ribbons and found that, after an initial transition, and within the temperature range of 383–582K

($T_g=663\text{K}$) and at a constant tensile stress of 312 MPa the strain rate varies inversely with time. They also performed stress relaxation experiments and showed that the stress dependence of the strain rate obeyed a hyperbolic sine relationship (nonlinear). To further reconcile all data, especially those obtained from the initial transition, a threshold stress ($=39\pm 4\text{MPa}$) was introduced into the formulation, although the physical meaning of the threshold stress was unclear.

Most recently, Kawamura *et al* [12] studied the high-temperature deformation properties of a $\text{Zr}_{65}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}$ metallic glass with a wide range of T ($T_g=652\text{K}$, $T_x=757\text{K}$) produced by a melt spinning method. They found that, within $T_{tr} < T < T_g$, the alloy has a low strain rate sensitivity value ($m < 0.25$) and the tensile elongation was also low ($< 100\%$). Similar observations were also made in $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ metallic glasses. Specifically, at a test temperature of 560K ($T_g=578\text{--}597\text{K}$), the alloy has a low strain rate sensitivity of only 0.20 and tensile elongation $< 50\%$.

From the above results we can summarize that homogeneous deformation of metallic glasses at temperatures below T_g are characterized by a low strain rate sensitivity and corresponding low ductility ($< 100\%$). This is attributable to the fact that structural relaxation is still relatively difficult during deformation as a result of sluggish diffusion in this temperature range.

$T_g < T < T_x$ (supercooled liquid region, SLR)

As early as 1980, Homer and Eberhardt [15] reported the observation of superplasticity in an amorphous $\text{Pd}_{78.1}\text{Fe}_{5.1}\text{Si}_{16.8}$ alloy, in a ribbon form, ($T_g=668\text{K}$, $T_x=683\text{K}$) during non-isothermal creep experiments. In their experiments, test samples were rapidly heated to the maximum temperature of 698K under a constant load (range: 25–150 MPa). The resulted creep rate was rather high; for example, an applied stress of 150 MPa results in a creep rate of 0.5 s^{-1} . The strain rate sensitivity value was estimated to be about one, suggesting possible Newtonian flow. Since 698K is higher than T_x , the dispersion of $0.4\text{ }\mu\text{m}$ grains in amorphous matrix was observed in the alloy after superplastic deformation. It is of particularly importance to note that slow heating during creep testing resulted in the disappearance of superplasticity. This is apparently caused by the structural instability of this alloy, as indicated by a narrow ΔT ($=15^\circ\text{C}$), thus fast crystallization kinetics.

Zelenskiy *et al.* [16] studied the formability of amorphous $\text{Co}_{68}\text{Fe}_7\text{Ni}_{13}\text{Si}_7\text{B}_5$ ($T_g=836\text{K}$, $T_x=856\text{K}$) at temperatures between 773 and 913K. They observed large tensile ductility at a relatively fast strain rate of 10^{-2} s^{-1} within 823–853K (within SLR). Specifically, a maximum elongation of 180% was recorded at a corresponding minimum stress of about 150 MPa. However, strain rate sensitivity was not measured. Subsequent TEM microstructural examinations indicated that 853K annealing resulted in the precipitation of nanometer grains ($\sim 50\text{--}70\text{ nm}$) in the alloy. From these results, the authors argued that the presence of a large amount of grain/amorphous matrix interfacial area are necessary for the observed extended plasticity. However, as it will be discussed later that this is not universally true. In fact, several experimental evidences indicated the opposite [12, 15].

To further understand extended plasticity in metallic glasses, Khonik and Zelenskiy [17] analyzed the available mechanical data from a number of metallic glasses, including both metal-metal and metal-metalloid systems. They concluded that extended plasticity occurs in alloys with a large ΔT , typically several tens degrees. The larger is ΔT ($=T_x - T_g$), the larger is the tensile elongation, provided tests were conducted in SLR. This indicates the importance of having a high thermal stability in a metallic glass during deformation. They noticed also that a faster heating rate usually produced a larger elongation. Apparently, this is also associated with structural stability since a slower heating results in an earlier crystallization.

In studying the formability of a $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy, Inoue *et al* [18] reported that the alloy in the supercooled liquid range (480–520K) behaves like a Newtonian fluid, i.e., $m=1$. A tensile elongation of over 15,000% was recorded at 500K at a strain rate of 10^{-1} s^{-1} . However, a careful examination of their stress-strain rate data indicated that the strain rate sensitivity tends to decrease to less than one when testing temperature approaches T_x .

Kawamura *et al* [12] recently studied the high-temperature deformation of a $\text{Zr}_{65}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}$ metallic glass with a wide range of T ($T_g=652\text{K}$, $T_x=757\text{K}$). In supercooled liquid region, they found that plastic flow were strongly dependent on strain rate and the strain rate sensitivity value exceeded 0.8, but less than one. The high strain rate sensitivity produces a corresponding high tensile elongation. For example, a tensile elongation of 340% was obtained at a strain rate of $5 \times 10^{-2} \text{ s}^{-1}$ and at 673K. However, a true Newtonian behavior ($m=1$) was not observed in the alloy. Kawamura *et al* [12] further tested a $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ alloy prepared by rapid solidification. Within 560-620K, the alloy exhibits a similar deformation behavior to that of $\text{Zr}_{65}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}$, namely, a high-strain-rate-sensitivity value accompanied by extended tensile ductility in the supercooled liquid region. In contrast to $\text{Zr}_{65}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}$ which is non-Newtonian, $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ behaves like a true Newtonian fluid (i.e. $m=1$) under appropriate testing conditions. The difference in Newtonian behavior may be associated with the fact that $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ is thermally more stable than $\text{Zr}_{65}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}$ in the supercooled liquid state, as pointed out by Kawamura *et al* [12]. (T_g are 72 and 100K for $\text{Zr}_{65}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}$ and $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$, respectively.) Thus, $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ can retain its amorphous state during high-temperature deformation, whereas crystallization may have already taken place in $\text{Zr}_{65}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}$. This is indirectly indicated by the fact that the viscosity of $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ is about one order of magnitude lower than that of $\text{Zr}_{65}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}$.

Most recently, Nieh *et al* [19] characterized the superplastic behavior of a bulk $\text{Zr}-10\text{Al}-5\text{Ti}-17.9\text{Cu}-14.6\text{Ni}$ alloy, synthesized by drop casting, in the supercooled liquid region ($T_g=631-705\text{K}$, $T_x=729\text{K}$). The alloy was observed to exhibit a large tensile elongation in SLR; a maximum tensile elongation of over 600% was recorded at 698-713K at a high strain rate of 10^{-2} s^{-1} . Using both strain rate cycling and strain rate increase techniques, it was observed that the alloy did not behave like a Newtonian fluid. It was argued that the non-Newtonian behavior might be caused by the unstable structure of the alloy in the supercooled liquid region. Upon thermal exposure, and particularly under an external applied stress, the amorphous structure tends to crystallize and results in a mixture of crystalline-amorphous structure.

In summary, for homogeneous deformation, and especially deformation in the supercooled liquid region, both the observations of Newtonian viscous flow as well as non-Newtonian behaviour have been reported. Despite such discrepancy large tensile ductility has been universally obtained in BMG in the supercooled liquid region. For convenience, these results are summarized in Table 1.

Table 1 Data from some metallic glasses deformed in the supercooled liquid region

Alloys	T_g	T_x	m	Elongation	Ref.
$\text{Pd}_{78.1}\text{Fe}_{5.1}\text{Si}_{16}$	668K	683K	~ 1.0	N/A	[15]
$\text{Co}_{68}\text{Fe}_7\text{Ni}_{13}\text{Si}_7\text{B}_5$	836K	856K	N/A	180	[16]
$\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$	480K	520K	1	1,800	[20]
$\text{Zr}_{65}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}$	652K	757K	>0.8	340	[12]
$\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$	578–597K	651K	1.0	N/A	[12]
$\text{Ni}_{77.5}\text{Si}_{7.5}\text{B}_{15}$	N/A	N/A	1.09	N/A	[21]
$\text{Zr}_{52.5}\text{Al}_{10}\text{Ti}_5\text{Cu}_{17.9}\text{Ni}_{14.6}$	631-705	729	$\sim 0.6-0.7$	650	[19]

As mentioned earlier, it was difficult to examine the structure of highly deformed specimens using TEM or x-ray diffraction, because the tested samples necked down to nearly a point. Moreover, the mechanical tests were all performed in air, which caused serious oxidation of test samples. The presence of a diffraction pattern may be simply indicative of oxide layer formation. Therefore, the purpose of this paper is to carry out experiments in vacuum to eliminate surface oxide formation and to further perform structural analyses on deformed samples, especially using synchrotron x-ray technique. In this paper, we don't use the terminology "superplasticity" which

has been widely used for describing the deformation of polycrystalline alloys. To avoid confusion, “extended plasticity” are used instead.

EXPERIMENTS

The material used in the present study has a composition of Zr-10Al-5Ti-17.9Cu-14.6Ni. Zone-purified Zr bars (containing 12.3 appm O and 10 appm Hf), together with pure metal elements, were used as charge materials. The alloys were prepared by arc melting in inert gas, followed by drop casting into 7.0-mm-diameter by 7.2cm-long Cu molds. The details of fabrication of the alloy have been described previously [22]. The glass transition temperature as well as crystallization temperature (T_x), have been previously measured using differential scanning calorimetry (DSC) [23].

Tensile sheet specimens were fabricated from the as-cast material by means of electrical discharge machining. They had a gage length of 4.76 mm, a thickness of 1.27 mm and a width of 1.59 mm. To prevent sample oxidation during testing, a vacuum or controlled inert gas atmosphere must be used. Thus, tensile tests were conducted using an Instron machine equipped with a quartz tube, which can be either evacuated or back filled with inert gas. A test sample is indirectly heated by a susceptor, which is directly heated by induction heating. Two thermocouples - one attached to the end and another to the center of the tensile specimen, were used to monitor testing temperature during testing. Because of structural instability during testing of samples at high temperatures, special attention was paid to rapidly heat test samples to minimize crystallization. Constant cross head speed tests were performed at temperatures of 410-440°C (within the supercooled liquid region) at strain rates of 10^{-2} and 10^{-3} s $^{-1}$.

X-ray diffraction was performed on undeformed and deformed specimens. These specimens were measured on the Unicat beamline 33-ID at the Advanced Photon Source, Brookhaven. The x-ray beam was focused to an $\sim 0.2\text{mm} \times 0.1\text{mm}$ spot. A slit was then placed in the beam to further reduce the beam size to $50 \times 50 \mu\text{m}$. The sample was placed on an x-y-z stage in the center of a six-circle Kappa diffractometer and oriented so that the surface of the sample was at small $\sim 10^\circ$ angle to the incident beam. The diffraction pattern was collected initially with a CCD camera that intercepted an $\sim 30 \times 30^\circ$ fraction of solid angle. Measurements were made on all samples both near the fracture point and at various distances from the point.

MECHANICAL PROPERTIES

The stress-strain curves for the alloy at different temperatures at a strain rate of 10^{-2} s $^{-1}$ is shown in Fig. 1. A yield drop phenomenon is readily observed at 410°C. The yield drop phenomenon has also been observed previously in the same alloy tested in air [19]. The phenomenon was also studied by Kawamura *et al* [24] during testing of a $\text{Zr}_{65}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}$ metallic glass in the supercooled liquid region. Kawamura *et al* [25] argued that the yield drop was a ‘transient phenomenon’, caused by an initial increase in atomic mobility at high strain rates, but upon yielding, the atomic mobility decreases and structure relaxes. However, it may also be explained by the creation of excessive defects (free volume) upon straining. The yield drop disappears at a higher testing temperature (425 and 440°C), and the phenomenon is replaced with a gradual decrease in flow stress. This decrease in flow stress is partially resulted from a decrease in strain rate, as a result of constant crosshead speed test. It is noted that samples, which showed extended plasticity exhibit significant necking. In fact, some samples necked down nearly to a point. The final decrease in flow stress is partially, not a result of softening, but reduction in load bearing.

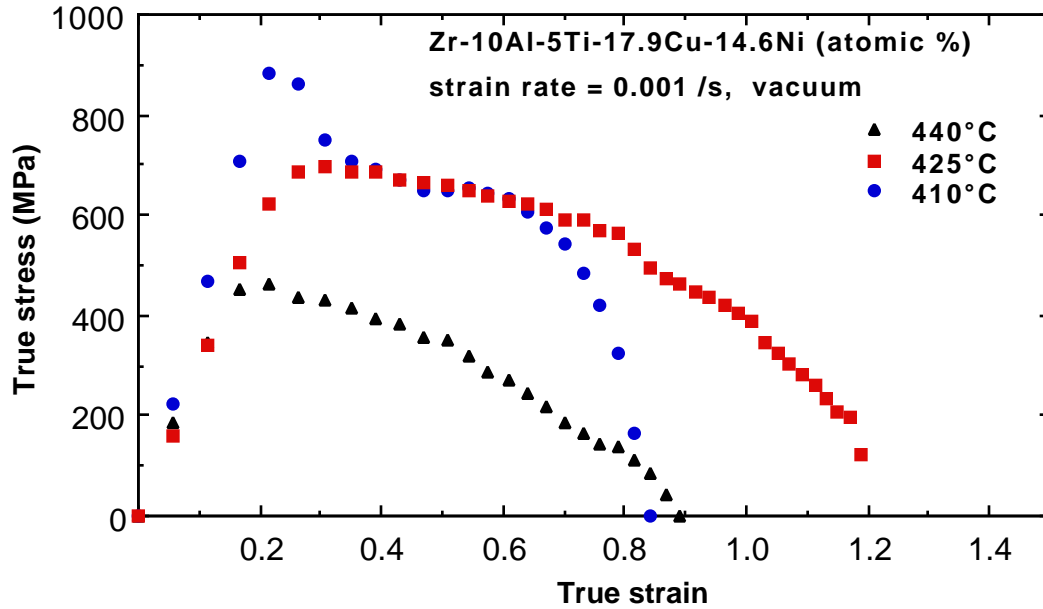


Fig. 1 Stress-strain curves of Zr-10Al-5Ti-17.9Cu-14.6Ni obtained at a strain rate of 10^{-2} s^{-1} in vacuum at temperatures near the supercooled liquid region.

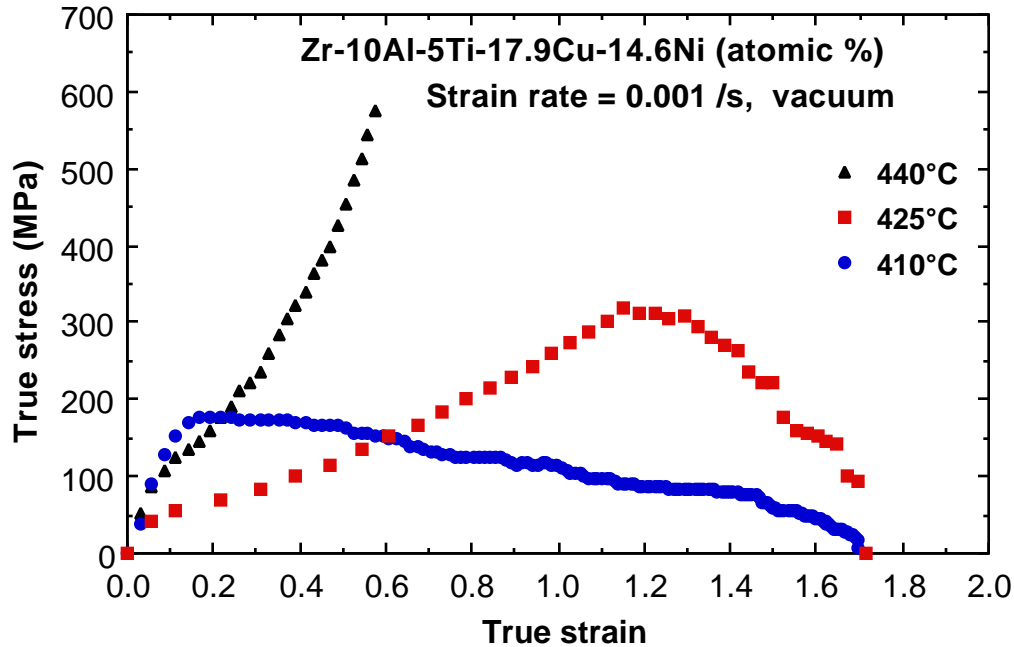


Fig. 2 Stress-strain curves of Zr-10Al-5Ti-17.9Cu-14.6Ni obtained at a strain rate of 10^{-3} s^{-1} in vacuum at temperatures near the supercooled liquid region.

The stress-strain curves for the alloy at different temperatures at a strain rate of 10^{-3} s^{-1} is shown in Fig. 2. At this strain rate, there is no apparent yield drop. At 410°C , the curve appears to

be “normal”, i.e. with a gradual decrease in flow stress. At 425°C, the flow stress begins with a value lower than that at 410°C but gradually increases, reaches the peak (~350MPa) at a relatively high strain value (~1.2), then reduces rapidly until fracture. At 440°C, the flow stress rapidly increases until reaching a high value of about 600MPa, at which point fracture occurs. The fracture strain was lower than that observed at the lower temperatures, and sample fractured in a brittle manner (Fig. 3).

To measure the strain rate sensitivity value, strain rate cycling tests were carried out at 410°C. The result is shown in Fig. 4; the values of strain rate sensitivity m in equation $\dot{\epsilon} = K \cdot \sigma^m$, where $\dot{\epsilon}$ is the strain rate, σ is the flow stress, and K is a constant, were measured by strain rate cycling between 10^{-2} and $7 \times 10^{-3} \text{ s}^{-1}$. There is no steady state region after each cycle, making it difficult to determine accurately the strain rate sensitivity value. This difficulty is associated with structural instabilities during testing. Specifically, despite the fact that 410°C is below the crystallization temperature, crystallized phase already evolved during the course of the test (see next section).

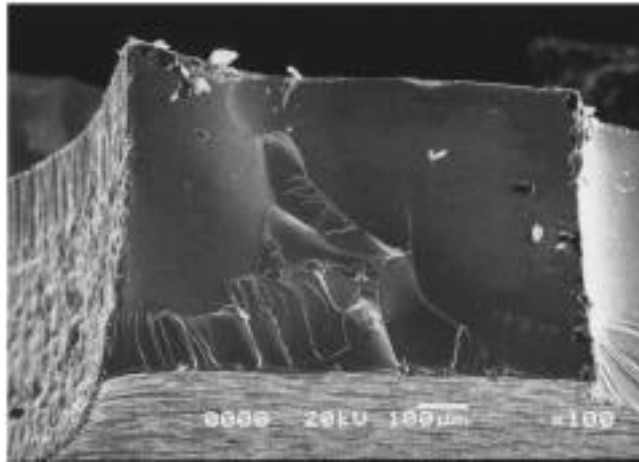


Fig. 3 Fracture surface of Zr-10Al-5Ti-17.9Cu-14.6Ni sample tested at 440°C and at a strain rate of 10^{-3} s^{-1} .

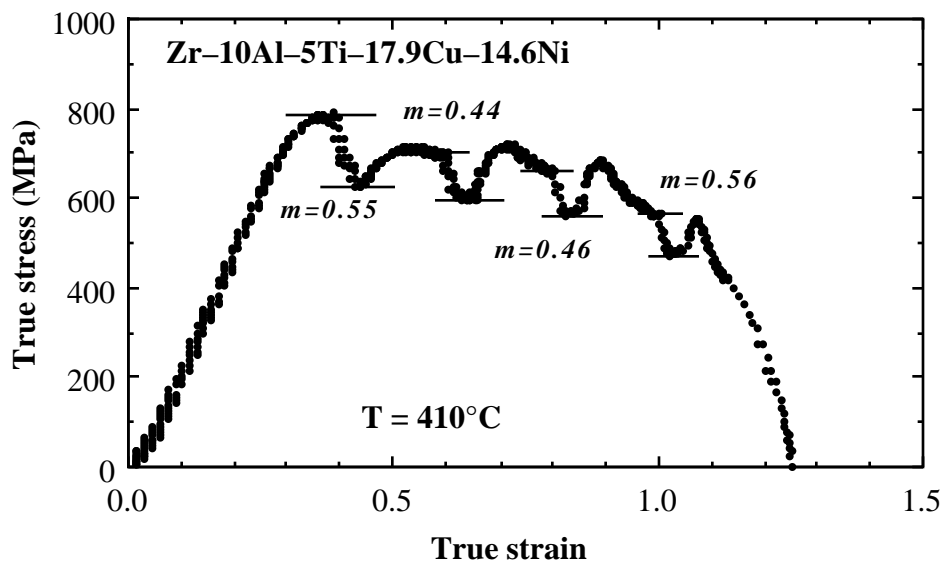


Fig. 4 Strain rate cycling test at 410°C showing that the strain rate sensitivity value is obviously less than unity.

As shown in Fig. 4, after each strain rate decrease, except for the first one, there is no steady-state flow region. The gradual decrease in flow stress after decreasing the strain rate may result from sample necking. It is worth noting that from Fig. 4 the "apparent" strain rate sensitivity for the present Zr-10Al-5Ti-17.9Cu-14.6Ni alloy is computed to be about 0.5. Although structural instability can contribute to some variations in determining the "true" strain rate sensitivity value, its influence is not expected to be sufficiently significant to imply a "true" strain rate sensitivity value of as high as one. In other words, the present alloy does *not* behave like a Newtonian fluid.

STRUCTURAL ANALYSIS

X-ray diffraction was performed on three specimens-as cast (undeformed), deformed at 440°C, and deformed at 410°C. The results are shown in Fig. 5. In the case of the 410°C specimen, an occasional sharp crystalline Debye ring was observed (Fig. 5b), but did not appear to be correlated to the distance from the tip. The crystalline size was estimated to be about 2.3nm. In the case of the 440°C specimen, the sample was clearly more crystalline (Fig. 5c), but crystal pattern appeared very uniform and was not correlated to distance to the surface. For the baseline comparison, measurements were also obtained from the as cast sample. This sample showed a clearly amorphous pattern over the entire sample with an occasional sharp crystalline Debye Ring that is believed to be due to a thin oxide layer or some surface contaminant (Fig. 5a).

The CCD detector was then removed and replaced by an analyzer crystal to obtain high-resolution measurements of the Debye rings of the 440°C specimen. The crystalline phase was identified to be primarily Zr_2Ni . Crystalline grains are estimated to be at least as large as 9 nm. It is consistent with that observed in the study of the crystallization of the alloy [23].

From the measurements it appears that the samples are undergoing a gradual amorphous to crystalline transformation uniformly as a function of processing temperature. The amount of strain does not appear to have a major influence on this process. These observations are consistent with the fact that testing at 410°C produces better results; at 440°C significant crystallization occurred and led to embrittlement.



Fig. 5 X-ray diffraction pattern from (a) as cast (undeformed), (b) deformed at 410°C, and (c) deformed at 440°C. Deformation strain rate = 10^{-2} s^{-1} .

Discussion

It is especially noted that ideal Newtonian viscous flow is actually an exception rather than the rule in the flow of viscous materials [26]. From a rheological viewpoint, the shear strain rate of a glass, $\dot{\gamma}$, is a nonlinear function of applied shear stress, τ , i.e.

$$\dot{\gamma} = f(\tau) \quad (1)$$

Assuming convergence, Equation (1) can be mathematically expanded into a Taylor series:

$$\dot{\gamma} = \sum_{i=1}^n A_i \tau^i = A_1 \tau + A_2 \tau^2 + A_3 \tau^3 + A_4 \tau^4 + A_5 \tau^5 + \dots \quad (2)$$

Each term in the above series has its own physical mechanism and can be identified with a specific, high-temperature, deformation process in polycrystalline solids, as listed in Table 2.

Table 2 Deformation mechanisms and ductility associated with each term in equation (2)

Coefficient	Mechanism	Approximate elongation, e
A_1	Newtonian viscous flow	unlimited
A_2	Grain-boundary sliding	$300\% < e < 8,000\%$
A_3	Viscous dislocation glide	$50\% < e < 300\%$
A_4	Dislocation climb	$e < 50\%$
A_5, A_6, A_7, \dots	Particle strengthening	$e < 10\%$

It is proposed that some metallic glasses do not behave like ideal Newtonian fluids in the supercooled liquid region is because of the concurrent operation of other deformation mechanisms resulting from the crystallization of fine structure. The presence of these new fine crystal regions is expected to trigger the operation of the high-order terms described in equation (2). For example, if an alloy contains regions of nanocrystalline grains, i.e. having a mixed nanocrystalline-plus-amorphous structure, as shown in Fig. 6a, then, to a first approximation, the total deformation rate can be expressed by:

$$\dot{\gamma}_{total} = (1 - f_v) \cdot \dot{\gamma}_{am} + f_v \cdot \dot{\gamma}_{cry} \quad (3)$$

where $\dot{\gamma}_{total}$ is the total strain rate, $\dot{\gamma}_{am}$ and $\dot{\gamma}_{cry}$ are the strain rates caused by the amorphous and crystalline phases, respectively, and f_v is the volume fraction of the crystalline phase. Since the plastic flow of an amorphous alloy can be described by $\dot{\gamma}_{am} = A\tau$, and the plastic flow of a nanocrystalline, superplastic alloy can be described by $\dot{\gamma}_{cry} = B\tau^2$, where τ is the flow stress, and A and B are material constants, equation (3) can be rewritten as:

$$\dot{\gamma}_{total} = (1 - f_v) \cdot A\tau + f_v \cdot B\tau^2 \quad (4)$$

It is obvious from equation (4) that the strain rate sensitivity, which is the reciprocal of the stress exponent, would fall between 0.5, the value for grain boundary sliding mechanism in fine-grained crystalline material, and unity, the value for Newtonian viscous flow.

However, if an alloy contains isolated nanocrystalline grains in its amorphous matrix (Fig. 6b), instead of having regions of nanocrystalline grains, its deformation behavior can also be treated in a similar manner. In this case, the total deformation rate can be expressed by:

$$\dot{\gamma}_{total} = (1 - f_v) \cdot A\tau + f_v \cdot B\tau^n \quad (5)$$

where $n > 5$, because the alloy can be treated as a dispersion strengthened solid. Obviously, the overall stress exponent for this alloy is greater than unity, i.e. $m < 1$.

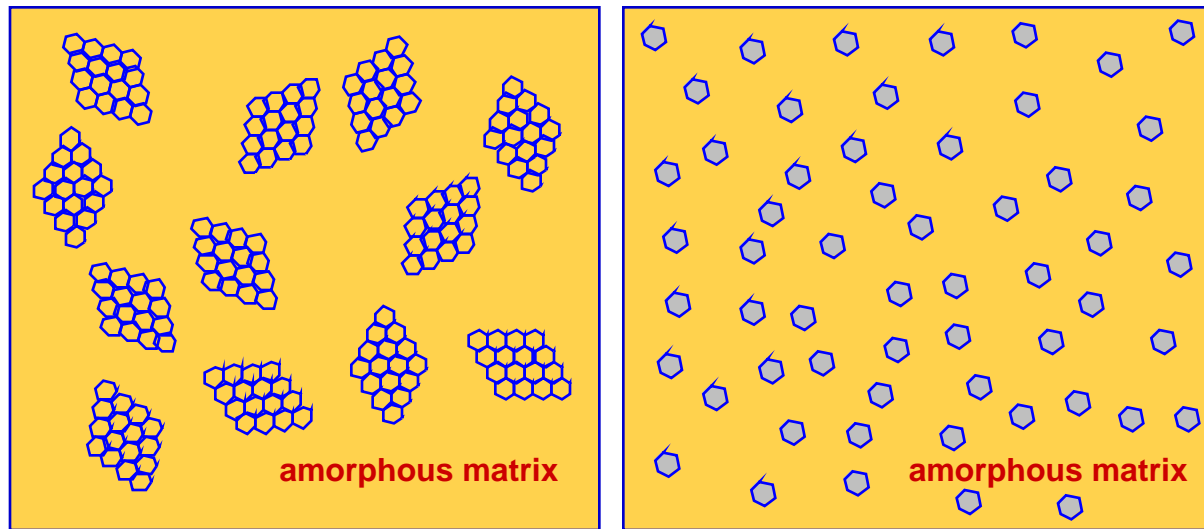


Fig. 6 Nanocrystallization of an amorphous alloy produces two types of nanocrystalline morphologies: (a) crystalline aggregates and (b) isolated crystals.

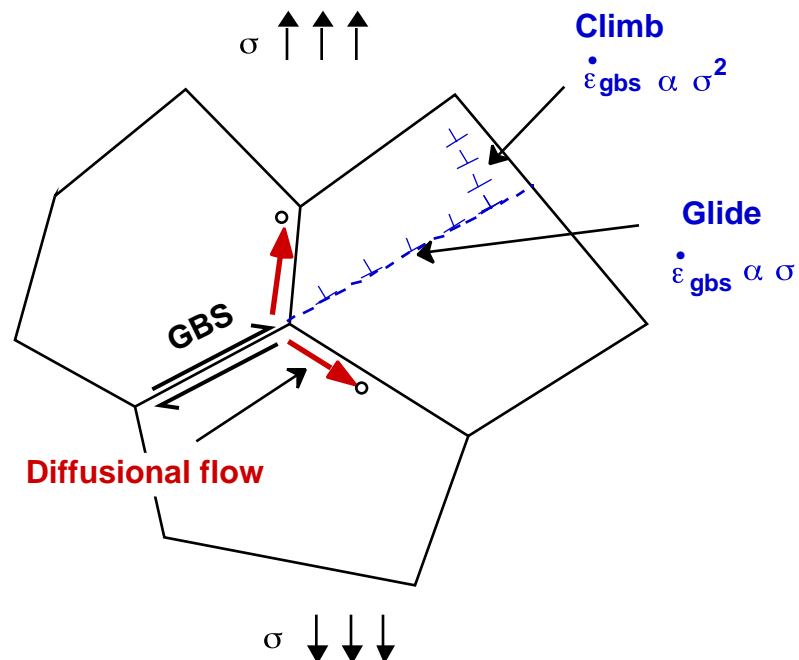


Fig. 7 Strain accommodation is necessary at grain triple junctions to prevent cavitation, which leads to fracture during superplastic deformation of fine-grained materials. The accommodation can take place through either a slip or diffusional process.

There is another peculiar issue, which is associated with the drastic decrease in tensile elongation in BMG at temperatures immediately above the crystallization temperature. For example, when a $\text{Zr}_{52.5}\text{Al}_{10}\text{Ti}_5\text{Cu}_{17.9}\text{Ni}_{14.6}$ alloy ($T_x = 729\text{K}$) was tested at 743K , the alloy exhibits practically zero ductility [19]. This appears to be in contrary to the conventional wisdom that a nano-grained alloy is expected to exhibit large elongation, presumably resulting from an extensive grain boundary sliding. However, it must be pointed out that, in the case of grain boundary sliding, sliding strain must be properly accommodated either by diffusional flow or by dislocation slip (e.g., climb or glide) across neighboring grains to prevent cavitation and, thus, fracture; this is schematically illustrated in Fig. 7. Dislocation slip in a multi-component, ordered intermetallic compound is expected to be not easy even at temperatures near T_x ($\sim 0.8 T_m$, where T_m is the melting point of the alloy).

On the other hand, when the grain size is sufficiently small, e.g. in the nanometer range, diffusion distance that is required for accommodation is also short. (Diffusional distance is estimated to be of the same scale as the grain size.) In such a case, the possibility of diffusional accommodation must be also considered. The criterion for the prevalence of diffusional accommodation can be estimated using equation:

$$\sqrt{D_b t} > d \quad (6)$$

where D_b is the grain-boundary self diffusivity, t is the time, and d is the grain size. Obviously, this equation favors a small grain size, slow strain rate, and fast diffusivity. If diffusional process is not sufficiently fast to accommodate sliding strain, especially at high strain rates. Cavitation would take place and fracture follows. This explains the observed low tensile elongation in some metallic glasses even they show a high m value at temperatures in the vicinity of T_x .

SUMMARY

Three main conclusions drawn from this study are:

1. Bulk metallic glasses generally have excellent mechanical formability in the supercooled liquid region.
2. Bulk metallic glasses may not be necessarily behave like a Newtonian fluid (i.e. $m=1$). The non-Newtonian behavior is associated with glass instability during deformation.
3. Multi-component Bulk metallic glasses can be used as the precursor of a nanocrystalline solid. However, the nanocrystalline solid is not necessarily superplastic. The non-superplastic behavior is caused by the difficult strain accommodation at grain triple junctions.

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